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16. ABSTRACT

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COMPARISON OF PHOTOCHEMICAL BEHAVIOR OF VARIOUS HUMIC SUBSTANCES IN WATER: I. SUNLIGHT INDUCED REACTIONS OF AQUATIC POLLUTANTS PHOTOSENSITIZED BY HUMIC SUBSTANCES

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ABSTRACT -- Humic substances are shown to photosensitize transformations of several types of synthethic chemicals that do not photoreact when exposed to sunlight in distilled water. In most cases, photoproducts were the same in colored natural waters and in solutions of soil-derived humic substances, including those obtained commercially. Kinetic studies in sunlight indicated that the efficiencies of the reactions photosensitized by humic substances of various origins were the same within a factor of 2.

INTRODUCTION

Photochemical reactions of pesticides and other commercially important chemicals have been investigated mainly in pure solvents such as methanol, hexane, or distilled water. In these solvents, photoreaction is initiated through direct absorption of light by the chemical, a type of photoreaction referred to as direct photolysis. Recent studies have indicated that some chemicals photolyze more rapidly in natural water samples than in distilled water (1-7). In some cases, compounds that are completely inert when exposed to sunlight in distilled water have been shown to photoreact rapidly in river or sea waters (3, 6). Accelerated photolysis in natural waters is attributable to reactions that are induced by various dissolved or suspended substances in the waters. These reactions compete with direct photolysis, changing both rates and photoproducts.

Aquatic humus is a widely distributed substance in inland and coastal water bodies (8). That photoreaction of 2,5-dimethylfuran (DMF) (6) occurs most rapidly in surface waters with high concentrations of aquatic humus suggests that humic substances are responsible for the enhanced photooxidation rate of this and possibly other compounds in natural waters. One explanation of the role of aquatic humus is that it "photosensitizes" reactions. Such reactions involve light absorption by the photosensitizer followed by interactions between electronically excited sensitizer molecules and the reactive substrate. Stated differently, a portion of the light energy absorbed by the humus is used to promote photoreactions that do not occur in distilled water. The photoreaction of DMF in natural waters was shown to involve a rapid intermediate step in which energy absorbed by humic substances was transferred to molecular oxygen to form singlet oxygen, which then oxidized the DMF (6). Mill and co-workers (7) have recently reported the light-induced free radical oxidation of several organic chemicals in natural waters; these reactions also possibly involved humic substances in the water. Aside from these studies, little is known about the photosensitizing capacities of various humic substances. Moreover, no attempts have been made to identify model substances that photosensitize reactions with efficiencies similar to those observed with the humic substances in aquatic environments.

In this and an accompanying paper, we present quantitative kinetic data that are used to compare photosensitizing efficiencies of several soil-derived humic substances and aquatic humus using DMF, disulfoton, aniline, and cis-1,3-pentadiene as substrates that undergo different types of sensitized photoreactions. Several commercial humic and fulvic acids are examined as model photosensitizers, and kinetic data are compared concerning photosensitized oxidation in water samples from black water systems in various parts of the United States. Results of this study can be used in devising procedures that provide an estimate of the transformation rates of chemicals that enter the aquatic environment.

EXPERIMENTAL

Materials. The commercial humic acids were obtained from the Aldrich Chemical Co., Fluka AG (Switzerland), and Carl Roth (West Germany). The latter was obtained in two forms, "humic acid" and "sodium humate." Several lots of Fluka humic acid were obtained as a gift from Ciba-Geigy Ltd., Basel, Switzerland; others were purchased from the Columbia Organic Chemical Co. Natural water samples were obtained from the top meter of four water bodies in the United States and were refrigerated at 5°C prior to use. A fulvic acid isolated from Mattole soil, Petrolia, California, was obtained as a gift from Dr. W. R. Mabey, SRI International. A commercial fulvic acid was obtained from Contech E.T.C. Limited, Ottawa, Ontario, Canada. Aniline (99%), obtained from Chem Services Co., and disulfoton, obtained from the EPA Health Effects Research Laboratory, Research Triangle Park, North Carolina, were used without further purification. 2,5-Dimethylfuran (DMF) was obtained from Chemical Samples Co. and distilled prior to use. cis-1,3-Pentadiene (99%) and trans-1,3-pentadiene from the Chemical Samples Co. were used as received. A sample of the sulfoxide derived from disulfoton was obtained as a gift from Dr. William Draper, Utah State University, Logan, Utah. p-Trimethylammoniumbenzophenone chloride was obtained as a gift from Dr. Richard Hautala, University of Georgia, Athens, Georgia.

Equipment. Reaction mixtures containing DMF and aniline were analyzed by direct aqueous injection on a Micromeritics high pressure liquid chromatograph equipped with a UV detector. The column was packed with ODS-2 and water-acetonitrile mixtures were used as the mobile phase. Organic extracts of disulfoton reaction mixtures were analyzed using a Tracor MT-222 gas chromatograph equipped with a linearized ^{63}Ni electron capture detector. The columns were 2 meters long by 2 mm i.d. and packed with 1.95% OV-210-1.5% OV-17 on 80/100 Gas Chrom Q. Disulfoton photoproducts were identified using a Waters Associates Model 440 liquid chromatograph interfaced with a Finnigan 3200 mass spectrometer. cis and trans-Pentadiene were separated on a 6-meter long by 2-mm-i.d. GLC column packed with 20% 1,2,3-tris (2-cyanoethoxy)propane on Gas-Chrom RA.

Preparation of solutions. Most of the commercial humic acids were insoluble in distilled water. To solubilize the acids, the following procedure was used. Humic acid (0.050 g) was added to an aqueous solution (100 ml) containing 0.1% sodium hydroxide. The resulting mixture was stirred for 12 hours and then was centrifuged at 15,000 rpm in a Sorvall centrifuge at 25°C for one hour. The supernatant was then diluted 20-fold with distilled water. The resulting solution was adjusted to pH 6 by adding 0.1 N sulfuric acid dropwise. The fulvic acids were dissolved directly in distilled water, followed by adjustment to pH 6. The natural water samples were centrifuged at 25° as above to remove particulates. All the natural waters studied were obtained from "black water" systems. Through addition of distilled water, the optical densities of the humic acid solutions, the fulvic acid solutions, and the natural water samples were approximately matched; specifically, the optical density in a 1.00 cm cell was adjusted to 0.20 at 366 nm. These optically matched solutions were used in the sunlight studies described below.

Photoproduct studies. Product studies were conducted in Aucilla River water and in solutions of Aldrich and Fluka humic acids at pH 6.0. Characterization and spectral properties of the major products from the photooxygenation of DMF in natural waters are discussed elsewhere (6). cis-1,2- Diacetylethylene was also the major product observed in the solutions of humic and fulvic acids.

Disulfoton (1.0×10^{-5} M) was irradiated for one day by sunlight in air-saturated solutions of humic substances (20 mg organic carbon per liter) contained in erlenmeyer flasks made of borosilicate glass. After irradiation, the reaction mixture was poured through an XAD-4 column to extract the products and unreacted disulfoton. The XAD-4 was extracted by acetone followed by methylene chloride; the combined extracts were concentrated using a Kuderna-Danish apparatus. One product was apparent in the liquid chromatogram of the reaction mixture obtained on ODS-2 with acetonitrile-water as mobile phase. The product was isolated through preparative liquid chromatography. The infrared, nmr, and mass spectra of the product were identical to spectra of an authentic sample of disulfoton sulfoxide: NMR (CCl_4) δ 3.8-4.4 (m), δ 2.4-3.2 (m), δ1.0-1.5 (m); IR(KBr pellet) 2980, 2940, 1010, 960, 825, and 790 cm^{-1}; mass spectrum m/e (liquid chromatograph coupled with mass spectrometer) 291, 274, 213, 185, 157, 153, 129, 125 (base), 97.

Aniline (1.0×10^{-5} M) was irradiated by May sunlight in solutions of humic substances for 5 hours and the reaction mixture was analyzed by liquid chromatography (ODS-2, CH_3CN-H_2O mobile phase). Several very polar products that eluted with shorter retention times than aniline were apparent but these were not identified. A peak with longer retention time was shown to correspond to azobenzene. The yield of this product was lower in humic acid solutions than in Aucilla River water.

Liquid chromatographic analysis of irradiated solutions of cis-pentadiene (ODS-2, CH_3CN-H_2O, uv-detector at 220 nm) showed only one peak corresponding to the retention time of cis and trans-pentadiene, which were inseparable. Analysis by GLC on the 20% tris(2-cyanoethoxy)propane column indicated conversion to trans-pentadiene, which was identified by comparison of its retention time to that of a reference standard.

Procedures for photolysis studies. Similar procedures were followed in all of the kinetic studies in sunlight. For each chemical 1.0×10^{-5} M solutions were prepared in the air-saturated, optically matched humic acid solutions described above and in distilled water. Equal portions of the resulting solutions were added to 13-mm-o.d. pyrex cylindrical test tubes that were equipped with ground-glass stoppers or Teflon-lined Mininert caps. The tubes were then placed in a rack that permitted simultaneous irradiation of 15 tubes by sunlight. The test tubes were positioned with their axes pointing north-south and tilted at a 20 degree angle. Control studies employing chemical actinometer solutions in the tubes established that the contents of each tube received the same amount of sunlight. After exposure to sunlight, photolysis rate constants (k_p) were computed using eq. 1

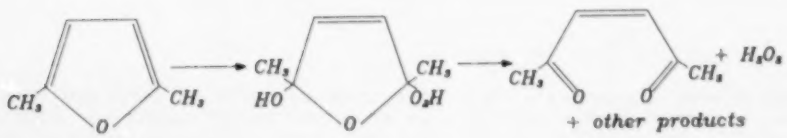
$$\ln \frac{P_o}{P} = k_p t \qquad (1)$$

where P_o and P were concentrations of the chemical at time zero and after exposure for time t. Dark controls were also monitored during the course of the experiments. No reaction in the dark was observed for any of the chemicals. DMF and 1,3-pentadiene were volatile so the experiments were conducted in tubes that were equipped with gas-tight Mininert caps and that were filled to the top to insure that the chemicals were predominantly in the aqueous rather than the vapor phase. The solutions of aniline and DMF were analyzed by direct injection into the liquid chromatograph. Disulfoton was extracted by an organic solvent containing an internal standard and then the extracts were analyzed by gas chromatography. The isomerization of pentadiene was followed by GLC analysis of the head space above the water after part of the solution was removed from the tubes. Controls showed that both isomers have the same Henry's Law constant within experimental error.

RESULTS AND DISCUSSION

To compare the influence of the various humic substances on photolysis of several organic chemicals, rate constants were computed for reactions that involve sunlight as the light source. The solutions of humic substances were optically matched to insure that the observed effects were solely attributable to differences in photosensitizing efficiencies. The reaction cell pathlengths of about 1 cm were sufficiently short that light attenuation reduced the photolysis rates by less than a factor of 2. In designing these experiments, chemicals were selected that were known to participate in several different types of photosensitized reactions (Figures 1 and 2). The photosensitized processes that were examined by use of these chemicals were oxygenation involving singlet molecular oxygen, hydrogen atom transfer, and energy transfer.

Photosensitized oxygenation. Photosensitized oxygenation was studied employing two chemicals, 2,5-dimethylfuran and the insecticide, disulfoton (Figure 1). Both of these chemicals were rapidly photooxidized in air-saturated natural water samples containing aquatic humus and in distilled water containing humic acids and fulvic acids. Previous studies established that the reactions of dimethylfuran in natural water samples are mediated by photochemically generated singlet oxygen (6). The same products, mainly diacetylethylene, formed in the solutions of humic and fulvic acids. The photosensitized oxidation of disulfoton, a sulfide, to the corresponding sulfoxide has previously been shown to occur in natural water samples by Draper and Crosby (4). In the present studies, the sulfoxide was also the major product in colored natural waters and solutions of soil-derived humic substances. Other studies have shown that singlet oxygen can oxidize organic sulfides to corresponding sulfoxides (9,10). That the reaction of disulfoton was about 30 times slower than that of dimethylfuran (normalized to equivalent light intensities) further indicated that both reactions occur with an intermediate step that involves singlet oxygen. Singlet oxygen reacts with diethyl sulfide, a compound that is structurally similar to disulfoton, about 0.05 times as fast as with dimethylfuran in protic solvents (11).



2,5-Dimethylfuron

Figure 1. Photoxygenations sensitized by humic substances in water.

Rate constants for the sensitized photooxidations of DMF and disulfoton were determined in sunlight at Athens, Georgia, under a variety of meteorological conditions during various times of the year. Photoreactions of DMF and disulfoton in distilled water were at least an order of magnitude slower than those in the solutions of humic substances (Table 1). No detectable reaction of either of these chemicals occurred in distilled water with exposure to summer sunlight for one day. Rate constants for photoreactions are directly proportional to the light intensity. To correct for the influence of variations in sunlight intensity chemical actinometers were exposed to sunlight at the same time and in the same way as the solutions of humic substances. Reactions of DMF or disulfoton in Aucilla River water were employed as actinometers. (Controlled studies in the laboratory (12) established that the photosensitizing efficiency of the substances in Aucilla River water remained constant during the period of these studies.) Results in Table 1 are reported as ratios of rate constants for reactions in the various solutions of humic substances to rate constants for the reaction in Aucilla River water. Remarkably, despite the diversity in origins of the humic substances, including several obtained commercially, the rate constants in all the solutions were within a factor of two of those for the Aucilla River solutions. Four lots of humic acid from Fluka AG had almost the same photosensitizing efficiency.

Table 1. Kinetic data for oxygenation reactions photosensitized by humic substances in water exposed to sunlight.

Humic Source	Relative Rate Constant[a,b,c] 2,5-Dimethylfuran[d]	Disulfoton[e]
Distilled Water	<0.01	<0.1
Aucilla River, FL	1.0	1.0
Okefenokee Swamp, GA	1.13 ± 0.32 (4)	--
Quincy Bog, NH	1.52 ± 0.08 (4)	--
Williamson River, OR	1.22 ± 0.40 (4)	--
Fulvic Acid, CA[f]	1.52 ± 0.40 (3)	1.2 ± 0.2 (3)
Contech Fulvic Acid[f,g]	0.98 (1)	1.1 ± 0.1 (2)
Aldrich Humic Acid[f,g]	1.21 ± 0.17 (6)	1.1 ± 0.4 (3)
Karl Roth Humic Acid[f,g]	0.50 ± 0.25 (4)	--
Fluka Humic Acid[f,g]		
Lot A	0.81 (1)	1.2 ± 0.4 (2)
Lot B	0.68 (1)	1.15 ± 0.4 (2)
Lot C	0.80 ± 0.14 (9)	1.30 ± 0.53 (5)
Lot D	0.80 ± 0.15 (4)	1.2 (1)

[a]Ratio of the sunlight photolysis rate constant to that observed for the photooxidation in Aucilla River water. [b]All solutions optically matched by adjusting absorbance to 0.20 (1.00 cm cell) at 366 nm. [c]Number of experiments in parentheses; each experiment involved triplicate kinetic runs for each solution. [d]Half-life in Aucilla River water ranged from about 20 minutes in winter to 5 to 10 minutes during summer at midday. [e]Half-life ranged from about 5 hours of midday sunlight during summer to 12 hours during winter. [f]Isolated from soils. [g]Obtained commercially.

Photosensitized reaction of aniline. Further studies were conducted to determine whether the humic and fulvic acids from commercial sources and the humic substances in a natural water sample photosensitized reactions of aniline. Aniline and its derivatives are known to undergo photosensitized reactions that involve hydrogen transfer from the nitrogen of the aniline to the sensitizer (13-15). Reaction products such as azobenzenes can result from coupling of the resulting anilino free radicals (13), and azobenzene was found to be a product in the present studies (Figure 2). It should be noted that,

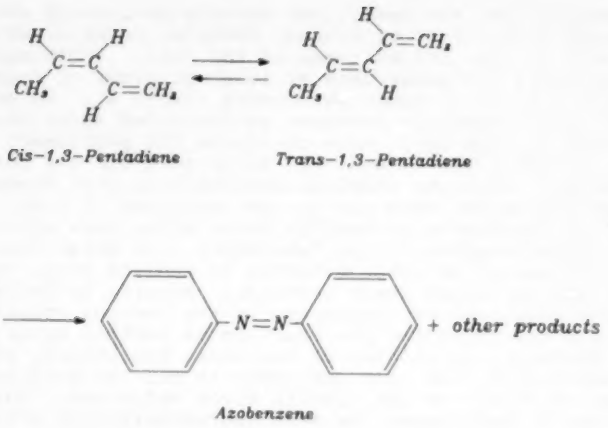


Figure 2. Reactions photosensitized by humic substances in water.

at the low concentrations of aniline employed here (1.0×10^{-5} M), the yield of azobenzene was very low in Aucilla River water (yield 0.2%) and even lower in the solutions of commercial humic substances. The data in Table 2 indicate that both the commercial humic acids and aquatic humus photosensitized the reaction of aniline with near-surface half-lives of 4 to 8 hours in May sunlight at Athens, Georgia. Aniline also photoreacted in distilled water, but at a much lower rate, i.e., a half-life of about one week. The commercial fulvic and humic acids photosensitized the aniline reaction at somewhat lower rates than that observed in the "black water" from the Aucilla River. The rate constants, however, were all within a factor of 2 of each other. Miller and co-workers (16) have obtained similar results in studies of the photosensitized reaction of 3,4-dichloroaniline, a metabolite of several important herbicides. Analysis of the kinetic data obtained in summer sunlight at Reno, Nevada, indicated that Fluka humic acid and the substances in several river or rice field water samples from California and Nevada photosensitized the reaction of dichloroaniline with about the same efficiency as observed for aniline in Athens, Georgia. Moreover, as in the present study, the yield of the coupling product, tetrachloroazobenzene, was higher with the natural water samples than with the commercial humic acid. Possibly, the commercial humic acids more effectively scavenge the intermediate anilino free radicals than does the dissolved organic matter in the natural waters. More detailed product studies would be required to clarify this point.

Photosensitized reaction involving energy transfer. Finally, the photosensitized isomerization of cis-1,3-pentadiene, a known acceptor in triplet energy transfer reactions (17), was studied in Aucilla River water and in solutions of humic acids (Figure 2). The concentration of cis-pentadiene was sufficiently dilute, less than 1.5×10^{-5} M, that the percent isomerization per unit time was concentration-independent. No detectable isomerization occurred when distilled water solutions of pentadiene were exposed to sunlight for one day. With the river water and humic acid solutions, isomerization proceeded to a photostationary mixture of 56% trans and 44% cis pentadiene. The same composition was observed when p-trimethylammoniumbenzophenone chloride, a known triplet energy donor for this reaction, was employed as the photosensitizer. The reaction achieves its photostationary state when the rate of the back reaction, photosensitized trans to cis-1,3-pentadiene, matches

Table 2. Photosensitized Reactions of Aniline in Sunlight[a] with Various Humic Substances as Sensitizers

Humic Source[b]	k_s, hr^{-1}	Relative Rate Constant
Aucilla River	0.17 ± .012	1.0
Aldrich Humic Acid	0.12 ± .0060	0.70
Fluka Humic Acid	0.091 ± .0080	0.54
Contech Fulvic Acid	0.11 ± 0.01	0.67

[a]Experiments conducted during May at Athens, Georgia. [b]Solutions of humic substances were optically matched by adjusting absorbance (1.00 cm pathlength) to 0.20 at 366nm; pH of humic acid solutions adjusted to 6.0 to match Aucilla River water.

that of the forward reaction. At dilute concentrations, the isomerization of pentadiene, a reversible reaction, can be described by eq. 2:

$$\ln \frac{t_\infty - t_t}{t_\infty - t_o} = - k_s t \qquad (2)$$

where t_∞ is the fraction of trans-isomer at steady state
t_o is the initial fraction trans
t_t is the fraction trans at time t
k_s is the first order rate constant

As with several of the other reactions studied, the humic acids were somewhat less efficient photosensitizers than the substances in the river water (Figure 3). More detailed studies of photosensitization by energy transfer will be described in a subsequent report.

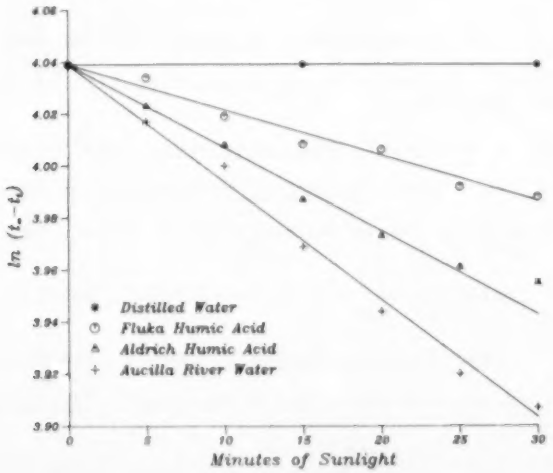


Figure 3. Kinetic data for isomerization of cis-1,3-pentadiene photosensitized by various humic substances in water on an overcast day (midday, July, Athens, GA). Symbols: t_∞ and t_t are fraction of diene isomerized to trans isomer at photostationary state and at time t, respectively.

CONCLUSIONS

This study provides additional evidence that natural substances in the aquatic environment can have important effects on photolysis rates of various types of organic chemicals. Humic substances were shown to play an important role in inducing these effects. Humic and fulvic acids extracted from soils photosensitize various types of reactions at similar rates to those observed in river waters containing comparable concentrations of humic substances. The photosensitizing efficiencies of the dissolved organic matter in several natural water samples from black water systems in various parts of the United States were found to be remarkably similar. Results of the studies indicate that several commercial humic or fulvic acids may serve as useful model photosensitizers in aqueous photolysis tests used in estimating environmental hazards of chemicals.

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DISCLAIMER

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